

Sediment–Water Column Exchange of Toxic Organic Compounds

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LONG-TERM GOAL

Our long-term goal is to understand the mechanisms of contaminant exchange between the seabed and the overlying water column and the long-term, system-wide dispersal of contaminants in contaminated harbors.

OBJECTIVES

The objectives of the study are

1. to quantify the rates and mechanisms of contaminant fluxes within harbor control volumes;
2. to improve methodologies for measurements of "bioavailable" hydrophobic contaminants;
3. to quantify the rate of contaminant exchange between particulate and dissolved phases; and
4. to develop a model for the role of resuspension on exposure of contaminants to the water column.

APPROACH

The organic-rich sediments of Naval harbors are major repositories of hydrophobic contaminants such as PAHs and PCBs; thus the exchange between the bed and the water column may be a major pathway for exposure of biota to contaminants as well as for export of contaminants from these sites. The study focuses on the Hudson River estuary, which exhibits highly variable suspended sediment concentrations due to variability of tidal resuspension. This variability allows us to quantify the influence of resuspension on the distribution and transport of contaminants.

A control volume has been defined for a 30-km section of the lower Hudson estuary, in which vigorous resuspension occurs in the estuarine turbidity maximum (ETM) region during spring tides. Measurements of physical variables and chemical concentrations are obtained north of, south of, and within the ETM. Moorings and bottom tripods provide measurements of currents, salinity, temperature, and suspended sediment concentrations as well as integrated measures of contaminants.

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Shipboard measurements include vertical profiles of chemical concentrations and water properties at selected time intervals. Sediment cores are also obtained throughout the estuary to determine sediment accumulation rates and reworking depths as well as to provide estimates of contaminant concentrations within the sediments.

Two levels of modeling are being accomplished, box modeling to constrain mass-balance estimates and determine the vertical and horizontal fluxes of contaminants, and three-dimensional modeling to obtain a process-level analysis of the mechanisms of vertical and horizontal exchange.

WORK COMPLETED

The analysis of the first field program has been completed, and staging for the second field effort is underway. The results of the first field program have lead to two publications in 2000. Rachel Adams completed her Masters Thesis, entitled "Sediment-Water Exchange of Polycyclic Aromatic Hydrocarbons in the Lower Hudson Estuary". Geyer was lead author on a paper submitted to *Estuaries* entitled "Sediment trapping and transport in the Hudson River."

RESULTS

A major advance in this project has been the development of Polyethylene Devices (PEDs) for the sampling of dissolved hydrophobic organic compounds (HOCs). These dissolved concentrations are of ecotoxicological concern as they reflect the HOC fraction that is driving uptake by the surrounding organisms. Laboratory studies of the uptake rate of different species of PAHs by PEDs indicate equilibration timescales of 1–3 days for phenanthrene and 7–20 days for pyrene. The range for each compound arises from the influence of temperature on the HOC diffusivities. Because the equilibrium timescale is long relative to tidal fluctuations, PEDs can be used effectively to average over tidal variations, thus providing a robust measure of the tidally averaged distributions of dissolved contaminants in harbors. Conventional measurements of these quantities would require intensive shipboard sampling and extraction procedures with less likelihood of achieving reliable tidal averages. The laboratory-measured polyethylene-water partition coefficients were 10^4 – 10^5 (mol/L_{PE})/(mol/L_w), allowing for the measurement of dissolved concentrations as low as 1 pg/L for benzo(a)pyrene and 400 pg/L for phenanthrene in the lower Hudson Estuary.

Measurements during the first field study in the Hudson Estuary revealed increased concentrations of dissolved pyrene and benzo(a)pyrene, but not phenanthrene, during increased sediment resuspension. These data suggest that resuspension events mostly influence the bed-to-water exchange of PAHs with greater hydrophobicities.

Observed concentrations of dissolved PAHs were far less than predicted assuming suspended solids equilibrated with the water and the concentrations were related via the product, $f_{om}K_{om}$, where f_{om} is the fraction of organic matter in the suspended sediments and K_{om} is the organic-matter-normalized solid-water partition coefficient for the PAH of concern. Adding the influence of soot to the partition model via $K_d = f_{om}K_{om} + f_{sc}K_{sc}$, where f_{sc} is the weight fraction of soot carbon in the solid phase and K_{sc} is the soot carbon-water partition coefficient estimated from activated carbon data, yielded predicted concentrations that were much closer to the observed values when PAH partitioning to soot was included in the partitioning model. This finding suggests that soot plays an important role in controlling the cycling of PAHs in the aquatic environment.

However, even when the soot partitioning of PAHs was included in the model, the predicted dissolved values were still larger than the measured values. This result indicated that the PAHs are not in particle-water sorptive equilibrium. This is explained by consideration of the timescale of interaction between estuarine water and resuspended particles. The water residence time in the lower estuary is approximately 2.5 days, and the fraction of time that there is significant resuspension is approximately 2 hours per tidal cycle. Thus the average contact with sediment of a particular water parcel is 10 hours. This timescale is shorter than the equilibration timescale of any of the measured PAHs, given the rate formula of Wu and Gschwend (1988) and the estimated particle characteristics. For phenanthrene, the equilibration timescale was 5 times as long as the particle contact time, whereas for benzo(a)pyrene the mismatch was a factor of 500, indicating extreme disequilibrium. These differences in desorption rates may explain in part the different spring–neap variations of the different chemicals.

In order to investigate if resuspended sediments are a source of PAHs to the water column, the ratio of phenanthrene-to-methylphenanthrene was calculated for the dissolved fraction and the total water column fraction. The total water column sample was predominantly composed of particle-bound PAHs. The phenanthrene/methylphenanthrene ratio for the dissolved fraction samples (measured with PEDs) was 0.2–0.5. The phenanthrene/methylphenanthrene ratio for the total (sorbed and dissolved) PAH extracts ranged from 0.96 to 1.75. These differences in phenanthrene/methylphenanthrene ratios suggest that sorbed PAHs have a larger pyrogenic source than the dissolved PAHs do.

IMPACT/APPLICATION

The development of the PEDs has potential application for estimating both water-column concentrations and exposure of biota to contaminants. This approach has valuable application both as a research tool and for monitoring of harbors.

The results of the Hudson study provide an important step in quantifying the role of resuspension in the transport of contaminants from the seabed to the overlying water column. They clearly indicate that non-equilibrium processes are critical to the desorption rate, and thus that the chemical transport rates and resuspension dynamics influence the fluxes of contaminants. These results will provide a testing ground for the development of numerical models of contaminant transport in harbors.

The varying ratios of petrogenic and pyrogenic PAHs in the dissolved and particulate fractions indicate that biotic exposure depends, not only on the mass of a contaminant in the environment, but also on its phase distribution. Contaminants attached to suspended particles may not be nearly as bio-available as their distribution coefficients would indicate, due both to the influence of soot and to the disequilibrium between dissolved and particulate forms.

TRANSITIONS

This research is likely to impact other research programs, monitoring and modeling activities as the results are disseminated.

RELATED PROJECTS

Geyer is receiving support from the Hudson River Foundation to study the sediment transport and trapping processes in the Hudson River estuary. Geyer is also receiving ONR support for modeling studies of sediment transport by river plumes during floods.

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